

T H E S I S

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AN INVESTIGATION OF THE
ALKALINITY OF SODIUM SULPHIDE
IN AQUEOUS SOLUTIONS.

AN INVESTIGATION OF THE ALKALINITY OF SODIUM
SULPHIDE IN AQUEOUS SOLUTIONS.

The use of sodium sulphide as an ingredient in the depilatory paint employed in the fellmongering of sheep-skins is now almost universal. The sodium sulphide is in aqueous solution and is customarily thickened by the suspension of slaked lime in the solution, sufficient lime being added to make a paint which will adhere easily to the skin. This paint is applied to the inner side of the skin and its depilatory action is such as to allow the easy removal of the wool from the pelt within 24 to 36 hours. It is recognised that care is necessary in the making up of this paint. If the sodium sulphide solution is too strong the pelt will be damaged; in extreme cases holes will appear, leading to a burnt skin, and such cases are most common in warm weather.

Although the active agent is sodium sulphide it is probable that the actual damage or burning of a skin is due to free alkali, whether present as an impurity in the commercial sulphide or formed by the hydrolysis of the sulphide.

Wilson (The Chemistry of Leather Manufacture. p. 284) to explain the mechanism of the sulphide depilation - states (1) there is a reaction between the protein keratin and the SH ion and (2) this reaction so alters the structure of the protein that the residues are more readily attacked by the

OH ion.

It was decided that an investigation of the alkalinity, hydrolysis, etc. of sodium sulphide would have some value.

The writer undertook to investigate the use of the hydrogen electrode in solutions of sodium sulphide in water, and in solutions of sodium sulphide to which had been added various other chemicals used in the manufacture of the depilatory paint.

Jellinek and Czerwinski, (Zeitschrift fur Physicalische Chemie, Band 102, 1922, pp. 438-279) regarded the hydrogen electrode as unsuitable for use in the sulphide solutions. They finally deduced the hydrogen ion concentration of sodium sulphide solution from the measurements of the other ions in the solution. Their results will be referred to later.

Furthermore there appears to be a prevalent belief that sulphide solutions would poison the hydrogen electrodes. (Wilson - The Chemistry of Leather Manufacture, p. 282. Fleass - The Journal of the Society of Chemistry in Industry, 1929. 152T. Atkin, Goldman and Thomson - The Journal of the International Society of Leather Trade Chemists, October 1933, p. 368.) Connected with this, no doubt, is the fact that H_2S is a catalytic poison for platinum in most reactions. A series of experiments, which will be described in due course, were performed in order to see if the electrodes were so poisoned as to affect the electromotive forces measured or, alternatively, to see if

poisoning occurred at all.

A certain amount of work on the alkalinity of sulphide solutions and paints was reported by Wright and Askew (New Zealand Journal of Science and Technology, vol. XI, No. 3, pp. 157-165, 1929) They simply titrated the solutions they investigated using (a) phenolphthalein and (b) methyl orange as indicators. They regarded the phenolphthalein end point titration as giving the free alkali and the methyl orange endpoint titration as giving the total alkali. These experiments were performed in connection with the introduction of calcium chloride in the depilatory paints as a means of controlling the alkalinity to eliminate the burning of pelts. The present writer therefore included a series of experiments with calcium chloride added to the sodium sulphide solutions to compare his results with those of Wright and Askew.

Finally the behaviour of the hydrogen electrode in a sample of commercially prepared depilatory paint was observed. The paint was kindly supplied by the New Zealand Refrigerating Company Limited.

No attempt was made to measure the more dilute lime-sodium sulphide solutions referred to in the leather trade as "Lime liquors". After the completion of the experimental work of this thesis a paper describing the gravimetric determination of the alkalinity of the lime liquors became available in New Zealand. (Atkin, Goldman and Thomson-- Journal of the International Society of Leather Trade Chemists. October 1933 pp. 368 et seq.)

PRELIMINARY EXPERIMENTS

A preliminary set of experiments was undertaken to see if the hydrogen electrode gave reasonable and reproducible results in the sulphide solutions and also in order to obtain some indication of the type of hydrogen electrode which was most likely to be of service. These preliminary experiments were performed at room temperature and a somewhat crude potentiometer was used to measure the E. M. F. These experiments sufficed to demonstrate that by using the Clark type of electrode vessel (vide infra) steady and definite potentials could be obtained from the cell $\text{Pt}|\text{H}_2| \text{Na}_2\text{S}_{(x)}|\text{KCl}_{\text{sat}}|\text{KCl}_{\text{sat}}|\text{HgCl}_{2\text{sat}}|\text{Hg}$. The Hildebrande type of electrode vessel was not so satisfactory nor could any definite results be obtained from Glasstone's type of hydrogen electrode. (Analyst, 1925 - 50 - 327)

Because these preliminary experiments were executed without either temperature control or accurate potentiometric apparatus, the results obtained are not incorporated in this work.

Description of the Apparatus.

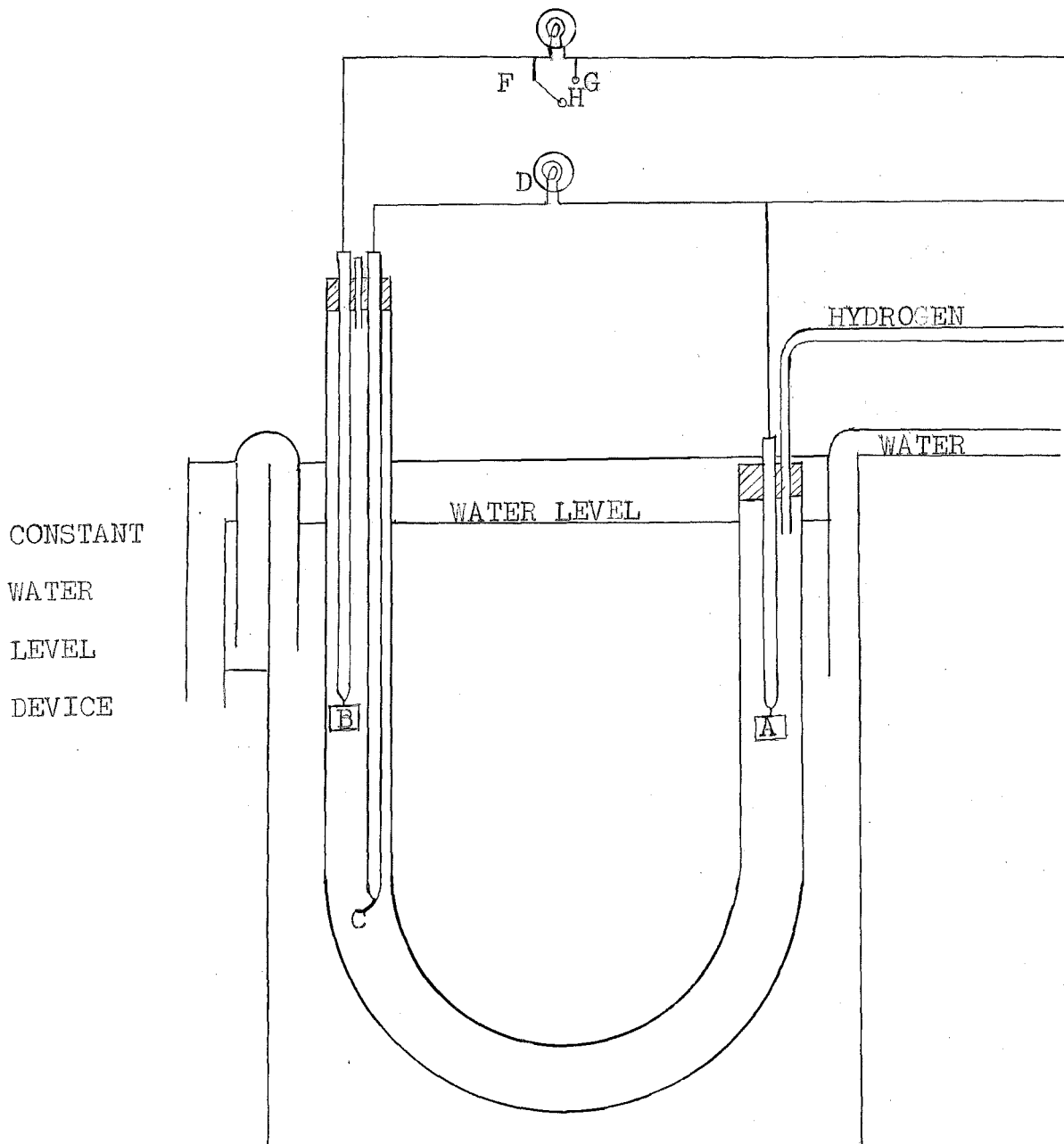
The Hydrogen Generator.

The hydrogen generator was of the Gaede-Niese type. It consisted of a U-tube of pyrex glass with an internal diameter of 1 inch. One arm of the tube was 8 inches long and the other was 12 inches long. The tube was fitted with two electrodes in the longer arm and one in the shorter arm. One electrode in each arm consisted of three square centimetres of platinum foil; the third electrode was placed lower in the tube (see fig. I) and consisted of two millimetres of platinum wire. All the electrodes were mounted in mercury filled glass tubes in the usual way. The U-tube was mounted in a large glass trough through which cold water flowed at constant level.

The generator was wired as shewn in figure I and the U-tube was filled to within an inch of the top of the short arm with 10% NaOH solution.

When the switch F was in the position H the electric current (220 volts D.C.) charged electrodes A and C negatively and B positively. Electrode C was provided with a small current through the resistance bulb D and also evolved a little hydrogen which ascended the longer arm as a stream of fine bubbles and "cleaned up" any oxygen which diffused down from the oxygen electrode. This scrubber electrode ensured that the hydrogen used was uncontaminated with the electrolytic oxygen.

FIG I



With the switch F in the position G the gas was more slowly evolved. When the gas pressure in the hydrogen arm increased the electrolyte was depressed in that arm and rose in the longer arm which was open to the air. This allowed a sufficient pressure of hydrogen to be obtained and also served to store enough hydrogen to flush the Clark electrode vessels.

The hydrogen was passed first through an empty wash-bottle which served as a trap for any liquid carried over from the generator and then through another wash bottle containing distilled water to adjust approximately the H_2O content of the Hydrogen to the water vapour pressure of the sulphide solutions. This approximation was considered to be close enough, for the sulphide solutions came in contact with about 5cc of the hydrogen. This last wash bottle also served to cleanse further the hydrogen.

Hydrogen Electrode Vessels.

The hydrogen electrode vessels were of the type designed by Clark in 1915 and described by him in "The Determination of Hydrogen Ions" pp. 293 and 294. Two of these vessels were used and both were connected with a KCl (saturated solution) bridge of the type customarily used with the Clark vessels. The hydrogen electrode vessels were rocked by the action of an eccentric pulley driven by an electric motor.

Calomel Electrodes.

A saturated calomel electrode of the common type was made and was standardised frequently by comparison with

freshly prepared 1/10N KCl, saturated calomel, electrodes.

Hydrogen Electrode Bases.

The hydrogen electrodes bases used in the greater part of this work were squares of thin platinum foil, about 25 sq. mm in area, mounted in glass tubes and lightly coated with platinum black. These were prepared and polarised in the usual way and require no comment. Various other types of electrode base were used. These will be discussed in the section dealing with the poisoning of the hydrogen electrode by the sulphide solutions.

Potentiometric Apparatus.

The potentiometer used for the first half of the experiments consisted of a metre bridge of platinum iridium wire in the Poggendorf circuit. This wire could be read accurately in divisions of less than .02ohms. The potential drop along this bridge was regulated to a value of 1.10 volts. The null point instrument was a Leeds Northrup needle galvanometer. By means of this apparatus the unknown E.M.F. was compared with that of an unsaturated cadmium cell which had a potential of 1.0183 volts.

For the second half of the experiments a Leeds Northrup student potentiometer became available and was used in conjunction with a mirror galvanometer and the same standard cell. Measurements of the potential of some of the cells measured by the metre bridge potentiometer were made with the student potentiometer. Both instruments gave the same readings.

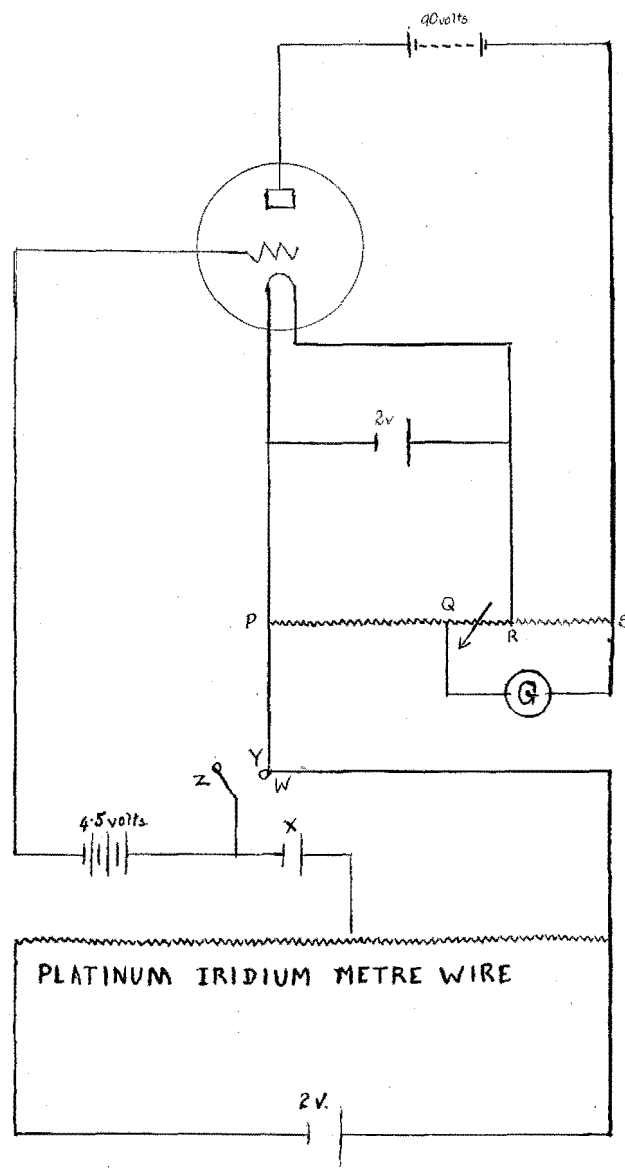
With both apparatus readings were recorded to .0002 volts.

Under circumstances to be described later another null point instrument was employed. This incorporated a thermionic valve. A slight modification of Goode's circuit was used. Fig. II illustrates the circuit. The three resistances represented by PQ, QR and RS were adjusted to balance out the plate current. PQ was a fixed resistance of 100 ohms and RS of 50 ohms. QR was a variable resistance of the carbon compression type (Lissenstat). All the other symbols in the diagram have their usual meaning. The plate current was first balanced out with the switch W in the position Y so that the galvanometer gave no deflection. The circuit was broken by placing W in the position Z and the meter bridge was adjusted till the galvanometer again gave no deflection. The cell X was either the standard cadmium cell or the cell being measured and the value of the cell being measured was calculated from the readings on the metre bridge in the usual manner. A slight grid current was detectable in this apparatus, but as the readings obtained with it were very close to those of the simpler Poggendorf arrangement, it was concluded that the grid current was insufficient to polarise the cells being measured.

Temperature Control Apparatus.

As the Clark electrode vessels are unsuitable for use submerged in liquids it was decided to construct a

FIG II



thermostatically controlled air bath. This was made in the form of a wooden box or cupboard with double walls and a double door. The hollow between the double walls was packed with wood wool. An inspection window was provided. The heating element was a 50 watt electric light bulb. This was controlled by a large chloroform filled regulator tube connected with a local six volt circuit. This local circuit operated a relay switch which in the 230 volt A.C. circuit connected to the heating bulb. A shield was placed to prevent direct radiations from the bulb reaching either the cells or the regulator. A four bladed fan of approximately 8" diameter was used to circulate the air in the air bath. It revolved at about 120 revolutions per minute. This was connected by pulley gears to the same motor which drove the rocking apparatus for the hydrogen electrodes. To eliminate electric leakage the interior of the bath was painted with hot paraffin wax. When carefully adjusted this bath appeared to be capable of keeping its temperature at $25^{\circ}\text{C} \pm 0.1^{\circ}$. A sensitive thermometer placed in a small beaker of liquid in the air bath shewed no discernible fluctuations in the temperature of the liquid once the temperature of 25°C was reached. The cooling apparatus suggested by Clark in his book "The Determination of Hydrogen Ions" was not constructed for, as was expected, the room temperature rose above 25 only twice during the summer.

Insulation, Assembly, Wiring, etc..

The potentiometric apparatus was all supported on

paraffin wax blocks or on paraffined plate glass. The electric wires from the various cells were kept as short as possible and all were insulated with elastic rubber tubing. This insulation was sufficiently efficient to render electric shielding of the apparatus unnecessary.

The hydrogen generator was mounted on top of the air bath, the potentiometer was mounted beside it and the motor for the fan beneath the air bath.

The hydrogen was led from the generator to the cells through glass tubing, with a rubber junction at the cell which provided sufficient flexibility to permit the rocking of the hydrogen electrode. The glass tube was used to prevent atmospheric oxygen diffusing into the hydrogen as it may when rubber tubes are used excessively.

PREPARATION OF THE SOLUTIONS MEASURED.

Preparation of the Sodium Sulphide Solutions.

The sodium sulphide solutions used in this work were prepared by dissolving sodium sulphide crystals of Analytical Reagent grade in freshly boiled distilled water. Solutions stronger than 1-molal shewed a tendency to turn brown in the presence of air; to overcome this these strong solutions were made up in a hydrogen atmosphere. None of the solutions were exposed to air unnecessarily, all were kept in well stoppered bottles and were used as fresh as possible. Each solution measured was analysed by the standard iodine-thiosulphate titration method and its composition calculated in terms of molality (gramme moles of solute per 1000 grammes of solvent).

Preparation of the Sulphide Solutions Containing Other Reagents

The sodium sulphide-calcium chloride solutions were prepared by adding to a solution of the sulphide prepared as described above a weighed quantity of the anhydrous chloride.

The sodium sulphide-sodium stearate solutions were prepared by adding to the sulphide solution a quantity of the soap solution of known strength. A series of solutions were made up in this way and the sodium sulphide concentration in each one was reduced to a constant value by the addition of the appropriate quantity of distilled water. These solutions were agitated for eight hours in

a mechanical shaker to break up the dense soap curd which formed.

The sodium sulphide-calcium hydroxide solutions were made up by adding excess lime to the sulphide solutions and then agitating the mixture for eight hours.

The sodium sulphide - sodium silicate solutions were made up by adding a weighed quantity of the silicate to the sulphide solutions.

The strength of the calcium chloride - sodium sulphide solutions was limited by the copious precipitate of calcium hydroxide formed. The addition of more than 5 grams of the chloride to 50 grams of a 1.35 molar solution of the sulphide produced a mixture too thick to manipulate in the electrode vessels.

The strength of the sodium stearate - sodium sulphide solutions was limited in a similar manner by the formation of a thick curd.

In neither the calcium chloride-sodium sulphide solutions nor the sodium stearate-sodium sulphide solutions was any attempt made to filter off the precipitate.

EXPERIMENTAL TECHNIQUE.

The technique described by Clark in "The Determination of Hydrogen Ions" pp. 294 et seq. was followed closely in the filling and manipulating of the cells using the Clark electrode vessels.

From each solution prepared two cells were made up and measured simultaneously. A new solution of the same concentration was prepared and duplicate cells made up from it. In this way four H.M.F. measurements were obtained from a sulphide solution of each concentration investigated. It will be seen that at least two different hydrogen electrode bases were used in the measurement of each concentration of sulphide solution. Before the H.M.F. of a cell was recorded for the purposes of this paper it was required that four readings obtained in this way should agree within 0.2 millivolts. The accuracy of the apparatus was checked frequently by the measurement of the E.M.F. of a cell containing a solution of known pH. The proprietary preparation "B.D.H. Universal Buffer" was used for this purpose.

The cells containing the sulphide solutions behaved in a somewhat peculiar manner. It was found that the E.M.F. of the cells rose to maximum after rocking had continued for about eight hours. This maximum potential, once attained, did not fall off as is so often the case with hydrogen electrode cells, but was maintained as long as the cell was kept rocking. One cell was rocked for nine hours

after the maximum E.M.F. had been attained and the potentiometer was unable to detect any variation in the E.M.F. during this time. The buffer solutions used to check the accuracy of the apparatus reached equilibrium with the hydrogen electrode in a few minutes and behaved generally in a normal manner. A possible explanation of this behaviour of the sulphide cells will be discussed later.

The maintenance of equilibrium by the sulphide cells enabled cells to be prepared and set rocking in the evening and then to be measured on the following morning. One pair of cells of a certain solution were usually measured after rocking under constant supervision during the day and the second pair of cells of the same concentration of solution were left overnight. Cells measured by this overnight method gave exactly the same results as cells which were under constant supervision.

When a cell had been measured the sulphide solution was blown from the electrode vessel by hydrogen and the KCl bridge was flushed with fresh KCl solution from the reservoir incorporated in the salt bridge. The electrode base was then washed with distilled water and the electrode vessel flushed with distilled water. The electrode vessel was filled with the next solution to be measured and again flushed with hydrogen. The cell was then ready to be prepared according to Clark's technique.

Experiments with Cells containing Very Dilute Solutions of
 Na_2S

The cells made up with very dilute solutions of sodium sulphide could not be made to give a definite E.M.F.. Even after twenty four hours no equilibrium could be attained. Some of the cells appeared to give a small E.M.F. but in these cases the results obtained from duplicate cells were far from agreement. It was thought that this might have been due to the resistance of the cells being sufficiently high to render the Poggendorf apparatus unserviceable, that is, with the apparatus used, the current passing through the cell when the electromotive forces were not balanced was insufficient to deflect the galvanometer.

To see if this were the case the apparatus previously described which incorporated a thermionic valve was used. This apparatus depended on the plate of the valve being charged when the potentials were unbalanced, so that there could be virtually no current passing through the cell. No satisfactory measurements of the E.M.F. of the dilute cells were made with this apparatus. No further attempts were made to measure the E.M.F. of the dilute cells.

The thermionic valve arrangement worked in a satisfactory manner for the cells containing stronger sulphide solutions, but it was somewhat difficult to use and had no advantages over the simpler Poggendorf apparatus when the latter was carefully used. The valve apparatus was used occasionally to verify the measurements made with the

usual potentiometer but was finally abandoned for the stronger cells when the more sensitive light ray galvanometer became available.

It is worthy of note that the valve apparatus functioned in a perfectly satisfactory manner when connected to any of the measureable cells through a 100,000 ohm resistance.

EXPERIMENTS TO INVESTIGATE THE EXISTENCE OR NON EXISTENCE
OF POISONING OF THE HYDROGEN ELECTRODES BY THE SULPHIDE
SOLUTIONS.

It was decided to perform a series of cell measurements on the sulphide solutions using widely different types of bases for the hydrogen electrode: this was acting on the supposition that if poisoning occurred it would affect the different types of electrode in different degree, and so the different types of electrode base would yield different E.M.F.'s in the same solution.

In these experiments the following types of electrode base were used:-

- (a) Bright platinum foil lightly coated with platinum black.
- (b) Bright platinum foil heavily coated with platinum black.
- (c) Pure gold lightly coated with platinum black.
- (d) Platinum gauze lightly coated with platinum black.
- (e) Lightly gilded glass lightly coated with platinum black.

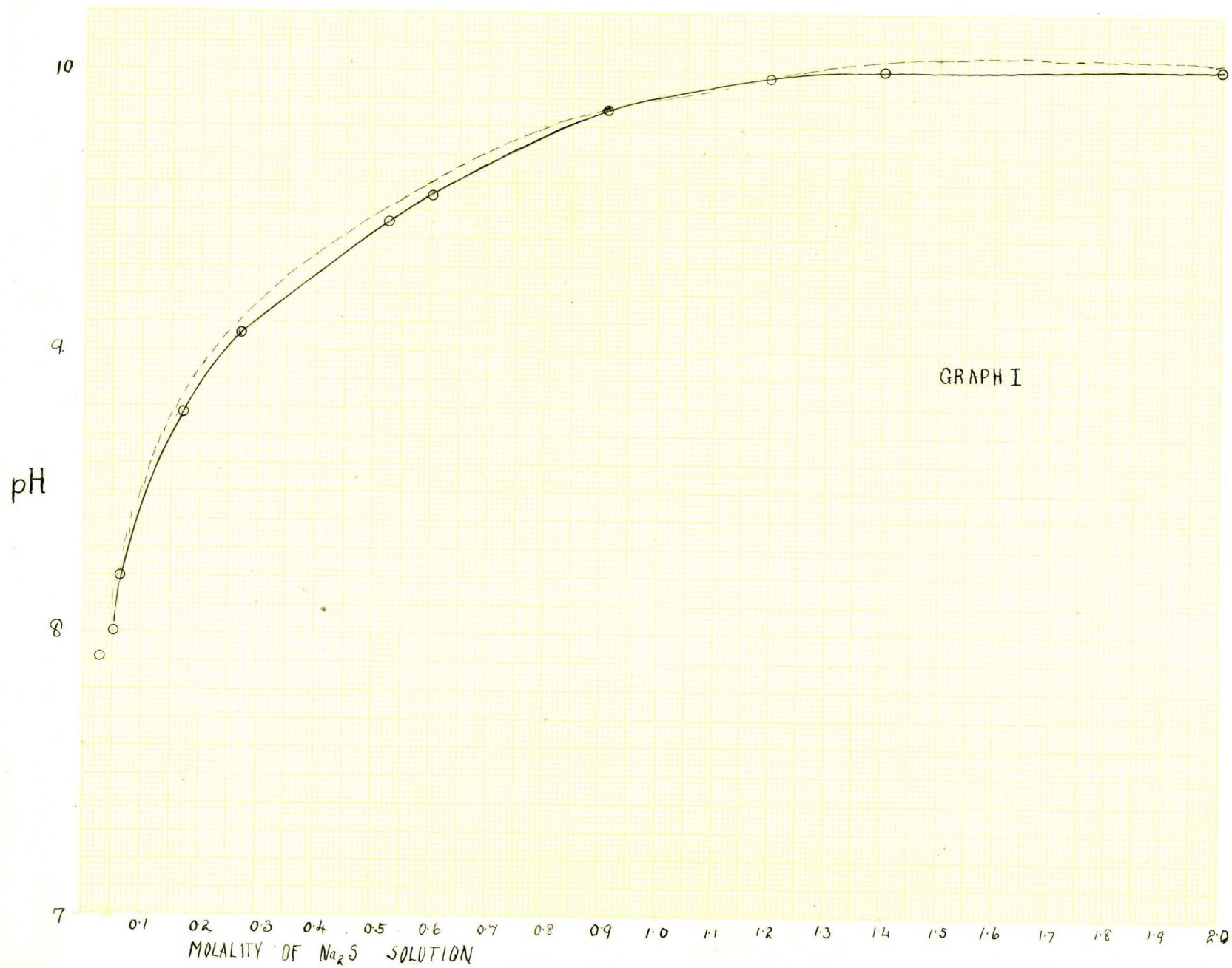
These different electrodes gave identical potentials in similar cells. This appeared to indicate that the electrodes were not poisoned. It was fully realised however that if the different types of electrode bases had given different potentials in solution it would have been fairly conclusive evidence that poisoning occurred but the most that could be deduced from the experiments was that

no evidence of poisoning was obtained.

The constancy of equilibrium attained when measuring the cells appeared to indicate that poisoning did not occur.

If the equilibrium attained in the cell was disturbed by any means, electrical or otherwise the former equilibrium was rapidly reattained.

It was concluded from the results of the experiments described above that no experimental evidence was obtained that the hydrogen electrodes were poisoned in the type of cell used.



RESULTS OF EXPERIMENTS MADE WITH CELLS CONTAINING AQUEOUS SOLUTIONS OF PURE SODIUM SULPHIDE.

The E.M.F. of the cell $\text{Pt} | \text{H}_2 | \text{Na}_2\text{S}_{(x)} | \text{KCl}_{\text{sat}} | \text{KCl}_{\text{sat}} | \text{HgCl}_{2\text{sat}} | \text{Hg}$ was measured. $\text{Na}_2\text{S}_{(x)}$ represents an aqueous solution of pure sodium sulphide of molality x .

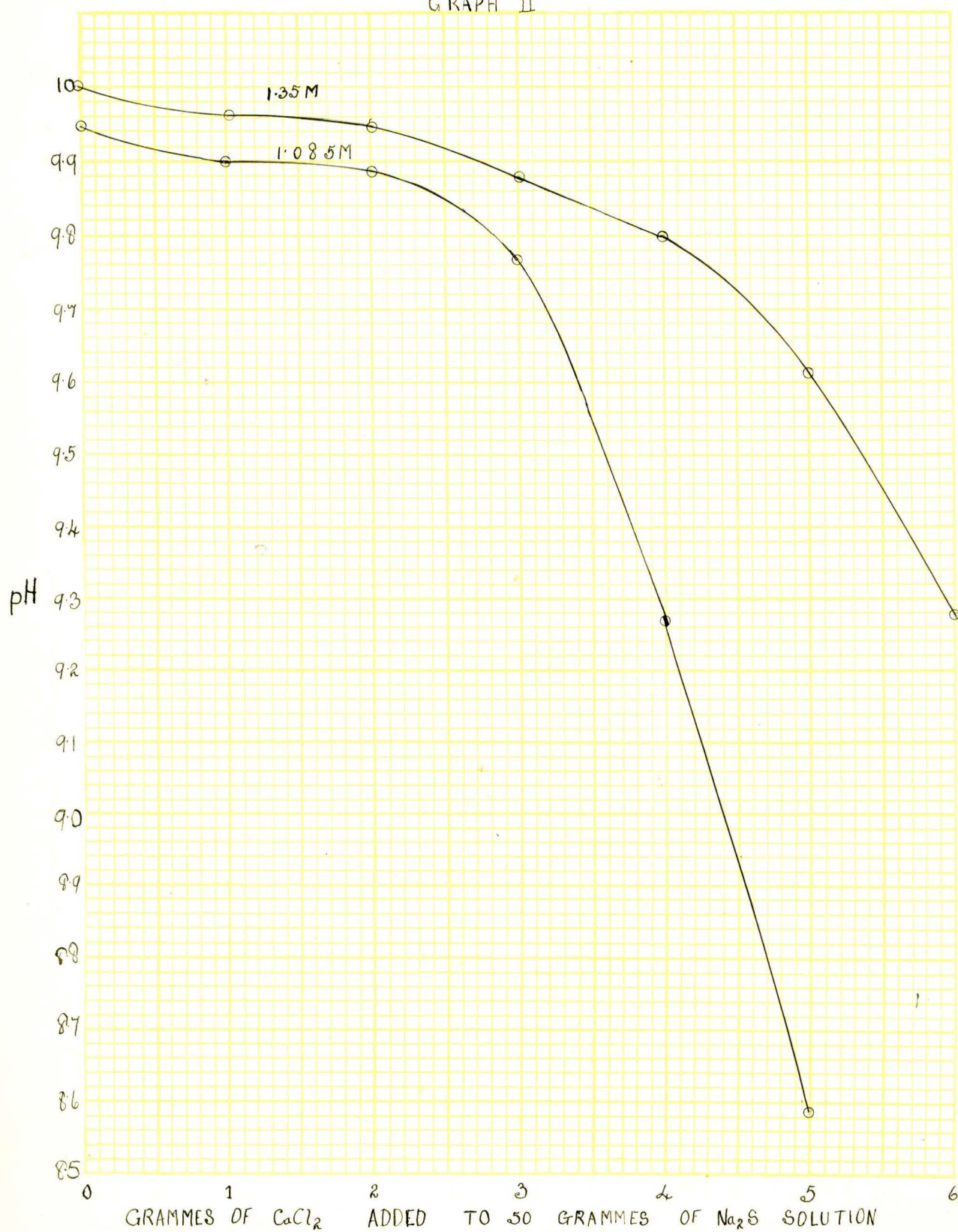
The pH of the solution of Na_2S was calculated from the usual equation :- $\text{pH} = \frac{E - E_{\text{cal}}}{0.059}$ where E is the measured E.M.F. of the cell and E_{cal} that of the calomel electrode used.

The results were as follows:-

<u>Molality</u>	<u>$E - E_{\text{cal}}$</u>	<u>pH</u>
2.00	.5906v.	10.01
1.40	.5900v.	10.00
1.217	.5897v.	9.995
0.91	.5817v.	9.86
0.604	.5649v.	9.56
0.5218	.5583v.	9.46
0.268	.5340v.	9.06
0.1685	.5180v.	8.78
0.06284	.4846v.	8.21
0.05	.4720v.	8.00
0.03	.4671v.	7.92

Solutions more dilute gave no reliable measurements.

GRAPH II



Results of experiments with solutions of Na_2S to which CaCl_2 had been added in various amounts.

Molality of the Sodium sulphide solution. = 1.085

Grammes of CaCl_2 added

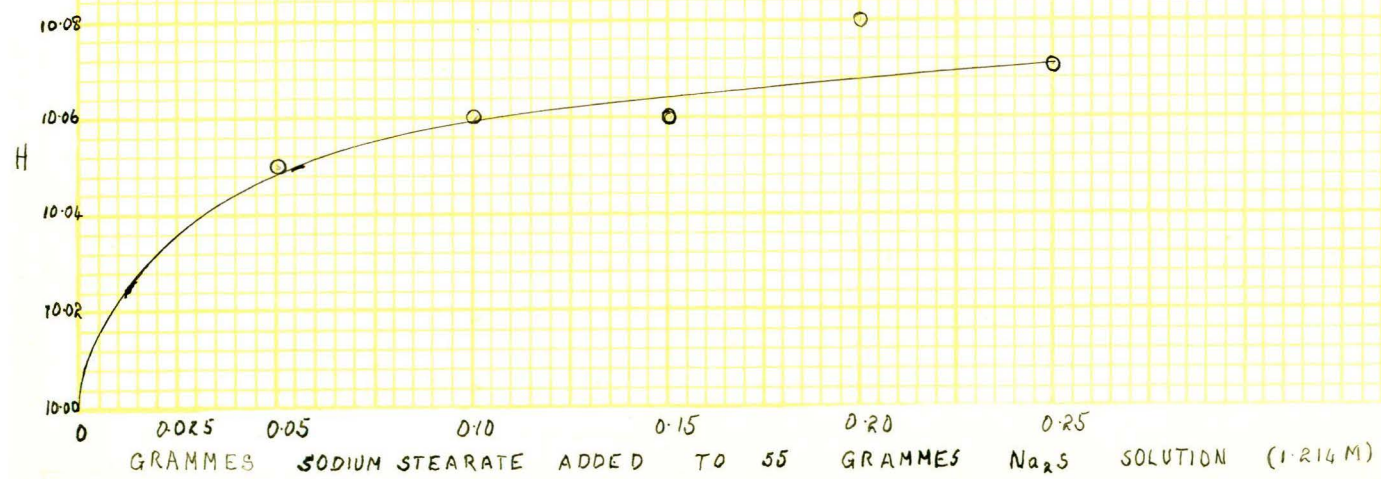
to 50 gms of Na_2S solution E - E cal. pH.

1.00	.5840v.	9.90
2.00	.5835v.	9.89
3.00	.5763v.	9.77
4.00	.5570v.	9.27
5.00	.5070v.	8.59

Molality of the Sodium sulphide solution = 1.35

1.00	.5882v.	9.96
2.00	.5870v.	9.95
3.00	.5820v.	9.88
4.00	.5784v.	9.80
5.00	.5680v.	9.62
6.00	.5476v.	9.28

GRAPH III



Result of experiments with solution of Na_2S to which sodium stearate had been added in varying amounts.

Molality of the Na_2S solution (corrected) = 1.214

<u>Grams of sodium stearate added to 55g. sulphide solution</u>	<u>E - E cal.</u>	<u>pH</u>
0.05	0.5930v.	10.05
0.10	0.5938v.	10.06
0.15	0.5935v.	10.06
0.20	0.5942v.	10.08
0.25	0.5942v.	10.07

Note:- Addition of more stearate to the sulphide solution produced a mixture too thick and curdy for manipulation.

Results of experiments with solution of Na_2S to which sodium silicate had been added in various amounts.

Molality of the Na_2S solutions = 1.085

Grams of sodium silicate
added to 55g. sulphide
solutions.

E - E cal.

pH.

1.00	.5850v.	9.92
2.00	.5850v.	9.92
3.00	.5850v.	9.92
4.00	.5850v.	9.92
5.00	.5816v.	9.86

Results of experiments with miscellaneous cells containing sulphide-lime mixtures.

- (1) 1.085 molal Na_2S solution holding in suspension excess $\text{Ca}(\text{OH})_2$.

$E - E_{\text{cal.}} = 0.5992\text{v.} \quad \therefore \text{pH} = 10.16$

- (2) Commercial sulphide depilatory paint consisting of a 1.40 molal (approx) solution of Na_2S which had been thickened with lime.

$E - E_{\text{cal.}} = 0.6075\text{v.} \quad \therefore \text{pH} = 10.30$

It is proposed to divide the discussion of the results into two sections:-

- (A) The discussion of the results tabulated on p.19 which refer to cells measuring the potential of the hydrogen electrode in pure solutions of sodium sulphide. In this section it is proposed to test the applicability of the usual physico-chemical equations to the equilibria existing in the aqueous solutions of sodium sulphide, and to endeavour to calculate any of the various constants which may apply to these solutions.
- (B) The discussion of the results tabulated on pp. 20-23 which refer to cells containing aqueous solutions of sodium sulphide to which other reagents had been added. These solutions, from their relation to the depilatory paints used in fellmongering practice, may be regarded as of a technical nature and will be regarded first from that point of view. Finally these "technical" cells will be considered to see if the measurements obtained can be used to show any light on problems of greater theoretical interest.

SECTION A

The results tabulated on page 19 are graphed (graph 1) plotting pH against molality. It was found that if the curve based on the equation $\text{pH} = 9.92 + 1.4 \log M - 1/25 M^3$ was also plotted it differed from the experimentally obtained curve in no place by more than 0.1 of a pH unit. In graph I the experimentally obtained curve is a solid line and that in accord with the equation is a dotted line. The curve given by the equation will not pass through the neutrality point when M becomes infinitely small but only holds through the range of experimental values. Further the term in M^3 becomes negligibly small below concentrations of 1.0 molal, hence the curve between the values of 1.0M. and 0.03M may be represented more simply by $\text{pH} = 9.92 + 1.4 \log M$.

In discussing the physico-chemical equilibria existing in aqueous solutions of sodium sulphide we are discussing the pH of the salt of a strong base and a weak acid. Hydrolysis must occur and it is from the point of view of hydrolysis that we shall first consider these results. For the purpose of this discussion, the hydration of ions will not be considered, and no distinction will be considered to exist between H^+ and H_3O^+ . It appeared to the present writer that with the information and figures available, to introduce the question of hydration would serve no useful purpose in this paper.

If we regard the pH (or in this case more properly the pOH)

as a measure of the concentration of the ion referred to, and change its form to an arithmetic function, then we may refer to it as a fraction of the greatest possible concentration of the same ion in the solution if the solution were completely hydrolysed. Such a fraction may be referred to as the fractional hydrolysis and is customarily denoted by the symbol x .

The objections to this are fairly powerful. In general these objections depend on the application of the activity concept to solutions of this type. According to this concept the pH as measured in the cells will depend on the activity of the hydrogen ion, not the true concentration of the ion. The activity of the ion may be considered as the concentration of the ion multiplied by a factor referred to as the activity coefficient of that ion. Also with all the other ions in the solution their effect on the equilibria existing in the solution will be that of the product of their respective activity coefficients and concentrations. If we accept the activity concept, as we must, it becomes practically impossible to distinguish between activities and concentrations of all the ions in solution, and so, in the light of the activity concept no value of x calculated as described above can have any real meaning as the "fractional hydrolysis". In the Transactions of the Faraday Society (August 1927) p. 513 T.M. Lowry definitely makes the statement that in the activity concept no measure of hydrolysis can have any real meaning.

In place of the simple hydrolysis equation for the salt of a strong univalent base and a weak univalent acid Pennyquick (Rept. Australasian Association for the Advancement of Science, vol. XVIII 1926, pp. 182-196) suggests the following equation as incorporating activity coefficients:-

$K_w/K_a = Cx^2/(1-x)\gamma_b/\gamma_s$ where γ_b and γ_s are the activity coefficients of the base and the salt respectively.

Such an equation adapted to the conditions of the solution we are considering would, no doubt, represent the state of affairs reasonably well but no figures are available here for γ_b or γ_s . In dilute solution the activity coefficients will tend to unity and the expression will simplify to the classical equation. This simplification can scarcely be expected to hold good over the range of solutions investigated in the present work. However it was considered advisable to make this assumption of unity of the activity coefficient in the case under consideration and to test the constancy of the "constants" so obtained. This will be dealt with in a later section.

In spite of these objections and for want of a more suitable expression the fractional hydrolysis x as defined at the head of this section was calculated: it seemed that this very simple expression would represent in itself the most satisfactory measure of the hydrolysis obtainable in this case.

The present writer suggests that x be not described as the fractional hydrolysis, but rather as the relative alkalinity

(relative acidity in the case of salts which hydrolyse to give an acid reaction). This description would beg the questions introduced with the activity concept, and would be a truer description of x .

It will be well at this stage to state the definition of x given by Pennycuik (*loc. cit.*). He states that the only exact meaning which can be assigned to x is such that cx will represent the unionised molecules of the acid formed by hydrolytic action.

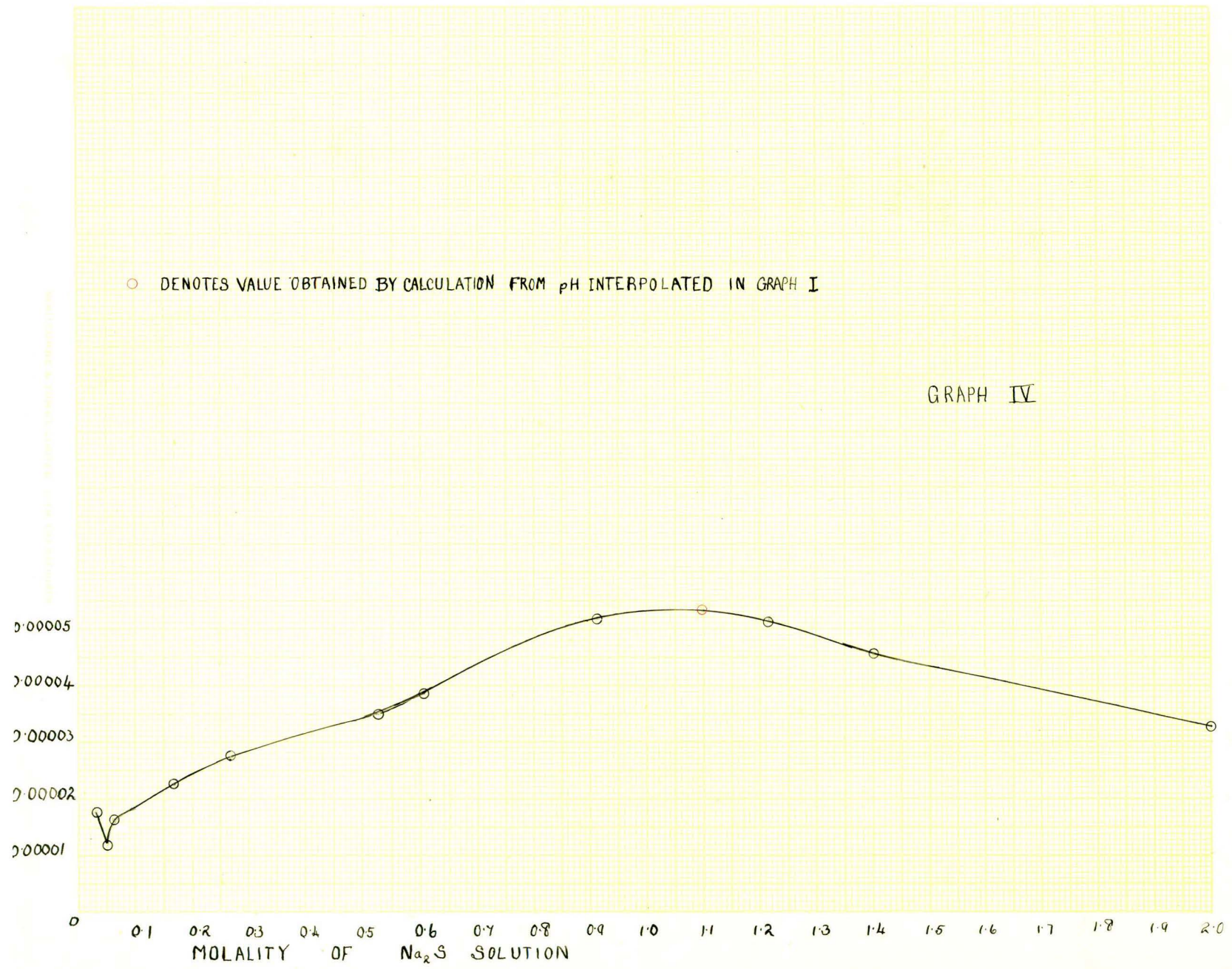


Table of the values of x calculated from the equation:-

$$x = \frac{(\text{OH})^{-20}}{C}$$

Where (OH) hydroxyl ion concentration as calculated from the classical equation and C is the molality of the solution. The calculations are based on the figures tabulated on page 19.

C	pH	x
2.00	10.01	0.0000326
1.40	10.00	0.0000455
1.217	9.995	0.0000518
0.91	9.86	0.0000507
0.604	9.56	0.0000383
0.5218	9.46	0.00003915
0.268	9.06	0.0000273
0.1685	8.78	0.00002276
0.06284	8.21	0.00001645
0.05	8.00	0.00001274
0.03	7.92	0.00001765

If we regard the hydrolysis as being governed by the equation



the value of x will be numerically double the above values which are based on the equilibrium:-



By making the assumption that the activity coefficients of the various ions present in solution are all unity we may simply deduce the expressions for the dissociation constant of H_2S and the Hydrolysis constant as follows, in the manner of the classical equations.

The progressive stages of hydrolysis may be represented by the following two purely stoichiometric equations:-



The mechanism of equation (1) may be represented by the two ionic equilibria:



which may be combined in the simple equilibrium equation:



Denoting Molar concentrations by square brackets we have from (1a) and (3):

$$[NaS^-] [H^+] = K_{a1} [NaSH] \dots\dots\dots(4)$$

$$[H^+] [OH^-] = K_w \dots\dots\dots(5)$$

and therefore:

$$[NaS^-] = \frac{K_{a1}}{K_w} [NaSH] [OH^-] \dots\dots\dots(6)$$

If we now make the simplifying assumptions that sodium sulphide and caustic soda are completely ionised according to the equations:



and if M denotes the molality of the total sodium sulphide (hydrolysed and non hydrolysed) and x the fractional amount hydrolysed according to equation (1) it follows from the foregoing equations and assumptions that:

$$[\text{NaS}^-] = M(1-x), [\text{NaSH}] = Mx = [\text{OH}^-]$$

whence from (6) we have:

$$\frac{M^2}{(1-x)} = \frac{K_W}{K_{a1}} = K_1 \dots \dots \dots (7)$$

The second stage hydrolysis is controlled by the equation:



which together with (5) yields the following equation:

$$[\text{S}^{--}] = \frac{K_{a2}}{K_W^2} [\text{H}_2\text{S}] [\text{OH}^-]^2$$

whence we obtain:

$$\frac{M^2 x^3}{1-x} = \frac{K_W^2}{4K_{a2}} = K_2 \dots \dots \dots (9)$$

The values of K_1 and K_2 calculated according to these two equations are tabulated on the next page.

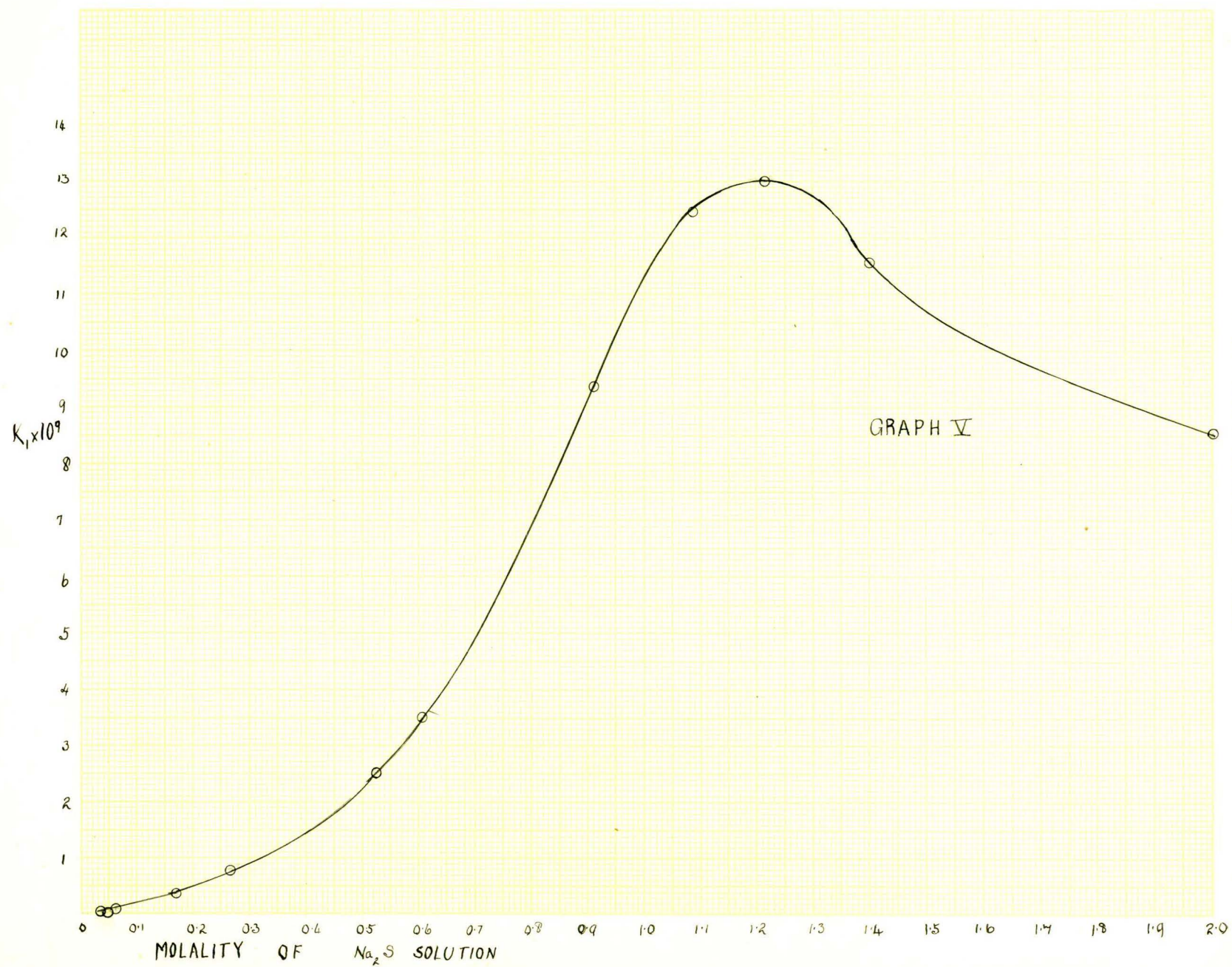
Note:- In the equation (9) $K_{a2} = \frac{[\text{H}^+]^2 [\text{S}^{--}]}{[\text{H}_2\text{S}]}$ not $\frac{[\text{H}^+] [\text{S}^{--}]}{[\text{HS}^-]}$

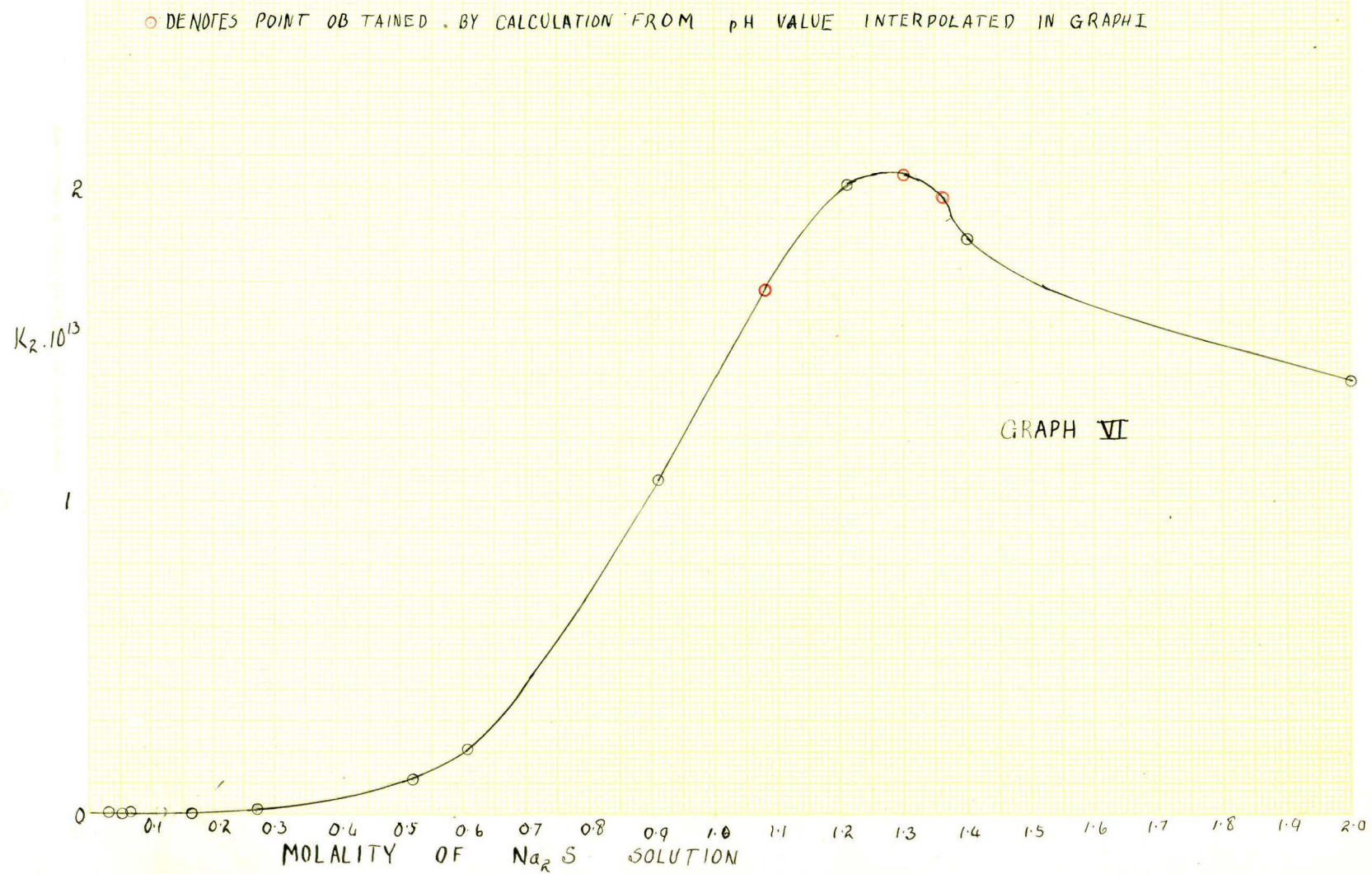
Table of the values of K_1 and K_2 for solutions of sodium sulphide calculated from the equations:-

$$K_1 = \frac{Mx^2}{(1-x)}$$

$$K_2 = \frac{M^2x^3}{(1-x)}$$

K_1	K_2	M
8.5×10^{-9}	1.385×10^{-13}	2.00
1.16×10^{-8}	1.84×10^{-13}	1.40
1.302×10^{-8}	2.015×10^{-13}	1.217
9.36×10^{-9}	1.07×10^{-13}	0.91
3.84×10^{-9}	2.05×10^{-14}	0.604
2.58×10^{-9}	1.18×10^{-14}	0.5218
8.00×10^{-10}	1.46×10^{-15}	0.268
3.50×10^{-10}	3.35×10^{-16}	0.1685
6.78×10^{-11}	2.11×10^{-17}	0.06284
3.25×10^{-11}	5.185×10^{-18}	0.05
3.73×10^{-11}	4.95×10^{-18}	0.03





From the equation $\text{pH} = 9.92 + 1.4 \log M - (1/25) M^3$ which approximately fits the experimentally obtained curve it is possible to deduce expressions shewing a simple relationship between molality and the quantities x , K_1 , K_2 , K_{a1} , and K_{a2} . in the more dilute solutions where the term in M^3 may be neglected.

We have for molalities less than 1 M.:-

$$\text{pH} = 9.92 + 1.4 \log M$$

$$\therefore \text{pOH} = 14.0 - 9.92 - 1.4 \log M$$

$$\therefore \text{pOH} = 4.08 - 1.4 \log M$$

$$\therefore (\text{OH}) = M^{1.4} / \text{antilog } 4.08 = M^{1.4} 12020^{-1}$$

$$\therefore x = M^{0.4} 12020^{-1} \text{ or } M^{0.4} 24040^{-1} \text{ as the case may be}$$

Now $K_1 = Mx^2/(1-x)$ and as x is very small K_1 may be regarded as equal to Mx^2 .

$$\therefore K_1 = M^{1.8} \cdot 12020^{-2}$$

$$\text{Similarly } K_2 = M^{3.2} \cdot 24040^{-3}$$

$$\therefore K_{a1} = 10^{-14} M^{-1.8} 12020^2$$

$$\text{and } K_{a2} = \frac{10^{-28} M^{-3.2} \cdot 24040^3}{4}$$

These relationships are of course very approximate and hold good only over a range of concentrations from 1.0 M to .03 M the most dilute solution whose pH was measured.

As was remarked before the curve given by the equation

$\text{pH} = 9.92 + 1.4 \log M - (1/25) M^3$ does not exactly fit the experimentally derived curve but only so closely as in no place to differ by more than 0.1 of a pH unit from the experimental curve.

From the results tabulated it may be seen that none of the values K_1 , K_2 , K_{a1} , K_{a2} has any constancy. This may indicate that none of the physico chemical equations used is applicable to aqueous solutions of sodium sulphide. That these equations are not applicable may be due to three causes. These are as follows:-

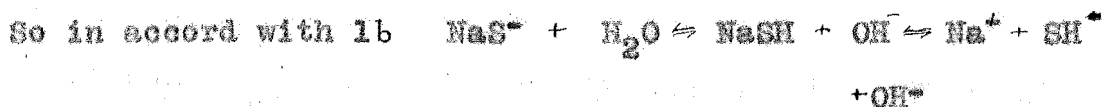
(a) The H_2S is more dissociated in the solution than is assumed in the equation $[NaSH] = [OH^-]$. If this equation is not true it is because the OH^- ion concentration in the solution is insufficiently greater than its concentration in pure water to make the equation valid. (c.f. Denham, The Electrometric Determination of the Hydrolysis of Salts, Trans. Chem. Soc. 1908, 93 p. 43.)

(b) The solutions are insufficiently dilute to justify the assumption that the activity coefficients are equal to unity. As was mentioned on page 27 it is very improbable that the activity coefficients should equal unity over the range measured.

(c) Equation 1a P. 30 probably does not represent the only possible equilibrium



It is probable we also have $NaSH \rightleftharpoons Na^+ + SH^-$



$$\therefore [OH^-] = [NaSH] + [SH^-]$$

So from we obtain

$$\frac{x}{1-x} [NaSH] = \frac{K_w}{K_{a1}} = K_1$$

If this is so K_1 will not be calculable from the pH figures, and so the inconstant results are not surprising.

Examination of graphs V and VI where K_1 and K_2 respectively are plotted against the molality of the solution shews that both graphs shew distinct trends, each rising to a maximum at the same concentration and each falling in a steep but even curve from that maximum.

In graph IV where we have x plotted against molality we find a maximum again occurring at the same concentration.

These maxima all occur at a concentration of about 1.2 M. The most that can definitely be inferred from the graphs is that something takes place at 1.2 M. which affects K_1 , K_2 and x .

It appears clear that this which takes place at 1.2 M. is represented in the equation $\text{pH} = 9.92 + 1.4 \log M - (1/25)M^3$ by the last term $(1/25)M^3$.

The following values of $\frac{[H^+][HS^-]}{[H_2S]} = K_{a1}$ have been obtained

from "Theoretical and Inorganic Chemistry" J. Meller Vol. X
P. 127

K_{a1}	Authority	Temperature
$10^{-7.04}$	Auerbach & Hlasco	18°C
10^{-7}	Jellinek & Czerwinski	0°C
$10^{-6.76}$	J. Walker & W. Cormack	10°C
$10^{-7.8}$	T. Paul	?

The value of $K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}$ is given by Jellinek and

Czerwinski (loc. cit) as 10^{-15}

From equation (8) P. 31

$$K_{a2} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]} = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+][S^{2-}]}{[HS^-]} = K_{a1} K_{a2}$$

So from the above results K_{a2} of the order of 10^{-22}

and so from equation (9) at 1 M.

$$\frac{3}{1-x} = \frac{10^{-28}}{4 \cdot 10^{-22}}$$

$\therefore x = .008$ if hydrolysis proceeds to the second stage
in accordance with equation (2) p. 30.

It is to be noted that the curve $pH = 9.92 - 1.4 \log M$
 $\frac{1}{25} M^3$ does not pass through the point $pH = 7$ at infinite
dilution ($\frac{1}{M} = \infty$) although we know that the pH at infinite
dilution must approximately be equal to 7. Hence it may
be inferred that a step must occur, at dilutions greater
than those measured, in the pH/molality graph, or rather

dH/dM must change at higher dilutions. This may indicate that at dilutions greater than those measured the associated ion NaS^- dissociates and hydrolysis in accordance with the second equation p.30 occurs. It may be significant that the plot of the lowest concentration measured seems to be to the left of the general pH/M graph. This may indicate the beginning of the change in dH/dM or it may indicate simply the commencement of the phenomena which render the hydrogen electrode unserviceable at high dilutions of Na_2S . It may be that the rendering useless of the hydrogen electrode, and the dissociation of the NaS^- ion are related phenomena.

Discussion of results.

Section B

This is a discussion of the results tabulated on pp. 20-23, which may be regarded as measurements of the pH of technical solutions.

Page 20 Solutions of sodium sulphide to which calcium chloride had been added. The first solution of sodium sulphide to which calcium chloride was added (1.085 M) was rather more dilute than the solutions used in depilatory paints, but it was thought that the results of adding the calcium chloride to a solution more dilute than that at which the maximum occurred in the K values would be interesting for comparative purposes. It is seen as should be expected that the quantity of calcium chloride required to reduce the pH a definite amount is much greater in a solution of the technical strength (1.35 M) than in the 1.085 M solution although the pH of each solution before the addition of the chloride was very little different. The results are incorporated in graph II. From these graphs the amount of calcium chloride required to reduce the alkalinity of the solutions of sodium sulphide may be read.

Wright and Askew (vid. sup.) make the statement that the addition of sufficient calcium chloride will render sodium sulphide solutions almost neutral to phenolphthalein. This is in agreement with the curves on graph V. Wright and Askew state that the great reduction in alkalinity can only take place in accordance with the equation:-



They conclude that if sufficient calcium chloride is added most of the sulphide present in solution will be present in the form of the sulphhydrate NaHS. Any free sodium hydroxide present will also react with the calcium chloride to form sodium chloride and calcium hydroxide. The amount of sulphide, determined by titration with standard iodine they found to be the same before and after the addition of the calcium chloride.

The present writer considers that the results of Wright and Askew lend much support to the view that the pH values of sulphide solutions determined by the hydrogen electrode are substantially correct.

Page 21 Reference to the graph of these results (graph III) shows that the addition of sodium stearate to the sulphide solutions tends to increase the alkalinity slightly. The curve of this increase is seen to be erratic, due no doubt, to varying conditions of curd formation in the mixture. This slightly erratic behaviour is sufficient to account for the unreliability of soap thickened solutions as depilatories which is known to exist in practical depilation. The maximum pH recorded in this series of experiments is not quite so high as that of a paint of known depilatory efficiency (vid.inf.).

Page 22 Reference to the table of these results shows the remarkable fact that the addition of sodium silicate to

a solution of sodium sulphide (1.085 M) does not increase the pH. It may well be that the hydrolysis and dissociation of sodium silicate and sodium stearate are similar in value.

Page 23 (1) For comparison with (2) a 1.085 M. solution of sodium sulphide was thickened with lime as for a depilatory paint. It is seen that the addition of lime increases the pH from 9.92 to 10.16 but that the increase is not sufficient to bring the pH up to the value of (2) a depilatory paint of standard composition and known efficiency. (2) was a simple depilatory paint suitable for winter conditions in New Zealand and consisted of a 1.4 M. solution of sodium sulphide thickened with lime. No calcium chloride had been added for the use of this reagent is confined to the summer months. The pH of this paint may be taken as that of a good paint of efficient depilatory action.

From the foregoing results it may be concluded that in the manufacture of sulphide depilatory paints the action of lime is to increase the pH and to act as a thickening agent. If the pH, from any cause, exceeds the value suitable for depilation it may be reduced by the addition of calcium chloride. The addition of sufficient calcium chloride will reduce the pH of sodium sulphide solutions almost to neutrality. Also that sodium stearate added as a thickener for paints will not raise the pH of the paint to that of a paint of known depilatory efficiency and the stearate also produces a paint of erratic pH value. The addition of sodium silicate to a paint does not appear likely to modify

the properties of the paint very much.

It will now be convenient to discuss critically the cell $\text{Pt}|\text{H}_2|\text{Na}_2\text{S}_{\text{sat}}|\text{KCl}_{\text{sat}}|\text{KCl}_{\text{sat}}|\text{HgCl}_{2\text{sat}}|\text{Hg}$. in the light of the results obtained. Firstly it appears clear from an abundance of literature that both H_2S and H_2 are adsorbed on platinum black. It appears at least possible that as the electrode in the Clark hydrogen electrode vessel is first immersed in sulphide solution it will form an adsorbed layer of H_2S . The electrode is next brought into contact with the hydrogen which displaces some of the sulphide solution from the cell, and is then alternately dipped in the sulphide solution and exposed to the hydrogen. As remarked previously the cell took about eight hours to come to equilibrium. It may well be that the hydrogen is capable of replacing the adsorbed H_2S on the platinum and that at the end of eight hours we have an electrode of platinum black saturated with hydrogen and functioning as a hydrogen electrode. The fact that there is agreement between the pH obtained by means of this electrode and that deduced from chemical evidence indicates that once the H_2S has been replaced the electrode functions in a normal manner.

Secondly a source of potential error is to be found at the liquid boundaries. No data is available of the potential existing at the boundary $\text{Na}_2\text{S}-\text{KCl}_{\text{sat}}$ and this may possibly be considerable. In the absence of data the usual practice of ignoring this boundary potential has been followed.

Thirdly there is the possibility of the formation of an

H_2S electrode in place of the hydrogen electrode. It appears clear that in some solutions the electrode Pt- H_2S can give a potential. (J.F. Daniell and V. Seets. Publication not known - see Moller Inorganic and Theoretical Chemistry Vol. X p. 127)

The argument that the pH values measured with the hydrogen electrode are in some agreement with the chemical work of Wright and Askew on sulphides may be used to show that the potential given by the H_2S electrode is not interfering with the hydrogen electrode sufficiently to invalidate its readings.

If we accept the view set forth at the head of this section that the hydrogen replaces the adsorbed H_2S we are no longer concerned with the potential of the H_2S electrode.

The following table is from the Zeitschrift für Physicalische Chemie-Band 102 - 1922- p.455. It is included in a paper entitled "Über die Dissoziation von H_2S , Na_2S , und $NaHS$, in wässriger Lösung."

Molekularkonzentrationen in Na_2S Lösungen bei ihrer Gefrier-temperatur.

Chem. Aquiv.	$H \cdot 10^{15}$
Na_2S pro Lit.	
2.85	8
2.12	4.2
1.59	4
1.06	4.8
0.53	7.5
0.21	15
0.10	30

From these results of Jellinek and Czerwinski's the value of x may be calculated as in the present work, x being the so-called fractional hydrolysis or relative alkalinity.

The results of calculating x are as follows:-

Normality ...	2.85	2.12	1.59	1.06	0.53	0.21	0.10
x	0.44	1.12	1.57	1.96	2.51	3.18	3.34

These results indicate that an aqueous solution of sodium sulphide is more alkaline than a solution of caustic soda of the same normality where the concentration is less than about

2.2 normal. If we accept x as the fractional hydrolysis we see by Jellinek and Caerwinski's figures the sodium sulphide solutions are more than 100% hydrolysed. Whichever way we regard these figures they appear to the present writer to be absurd.

SUMMARY

- (1) In a suitable apparatus the hydrogen electrode gives reasonable and reproducible results in aqueous solutions of sodium sulphide, provided the solution is not more dilute than 0.03 N.
- (2) There is no evidence that poisoning occurs.
- (3) There is some evidence that at concentrations above 1.2 N some phenomenon affects the values of pH, K_1 , K_2 etc.
- (4) The pH of aqueous solutions of sodium sulphide as calculated from measurements with the hydrogen electrode is related to the molality by the expression:-
$$\text{pH} = 9.92 + 1.4 \log M - 1/25 (M^3)$$
down to the lowest concentration measured (0.03 N).
- (5) The actions assumed in the fellmongering trade to occur when various reagents used in the manufacture of depilatory are added to pure sodium sulphide solutions are confirmed by hydrogen electrode measurements.